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Ceramics International 31 (2005) 177–180

CERAMICS INTERNATIONAL

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Water vapor corrosion of mullite containing small amount of sodium

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Received 12 January 2004; received in revised form 28 January 2004; accepted 10 March 2004

Abstract

The corrosion test for hot-pressed mullite bulk was performed in static state water vapor environment at higher temperatures such as 1300 and 1500 °C. After corrosion test, the samples exhibited weight gains with a rate of 6.60×10^{-6} and 8.42×10^{-5} g/cm^2 h at 1300 and 1500 °C, respectively. Microstructural and phase analyses revealed, corundum phase formed on mullite bulk surface and a large amount of pores were formed near the bulk surface. Crystalline corundum was directly grown from silica rich sodium containing aluminosilicate phase.

Keywords: B. Surface; C. Corrosion; D. Mullite; E. Thermal applications

1. Introduction

Mullite is a candidate material for high temperature application because of its stability and low thermal expansion coefficient. For the reason that the thermal expansion of mullite is very close to that of silicon carbide ceramics, mullite has been used as environmental barrier coating (EBC) material for SiC/SiC composites [1,2]. It has demonstrated that SiC/SiC composites with mullite EBC layer had very good water vapor corrosion resistance at above 1300 °C [1,2].

On the other hand, during hot corrosion of silicon nitride ceramics, silica phase is formed by the oxidization of silicon nitride and then, sodium silicate is formed by the reaction between silica and sodium oxide up to 1000 °C [3,4]. In these reports, they reported weight gain for the samples during hot corrosion test due to the oxidation of silicon nitride [3,4]. Later, Li et al. [5] suggested that mullite EBC layer on silicon nitride ceramics successfully protected from the alkali corrosion. However, they reported a weight loss for the sample up to 1000 °C. It does mean that mullite phase could sustain the water vapor corrosion even if sodium also exists in the environment. However, no detailed study of the water vapor corrosion for monolithic mullite phase above 1300 °C has been reported yet. Hence, in this report, the water vapor corrosion test was performed for mullite bulk at two different temperatures say, 1300 and 1500 °C, respectively, and the effect of small amount sodium on the water vapor corrosion mechanism was discussed.

2. Experimental

Al_2O_3 (99.99% purity with 0.001% sodium, High Purity Chemicals Co. Ltd.,) and SiO_2 (99.9% purity, High Purity Chemicals Co. Ltd., 0.8 μm particle size) powders were used as the starting materials. Al_2O_3 and SiO_2 in stoichiometric molar ratio of 3:2 were taken and homogeneously mixed in an agate mortar using ethanol. The mixed powder was packed in a graphite die and hot-pressed at 1600 °C for 3 h in Ar atmosphere under a pressure of 20 MPa. The sintered bulk was cut into specimens of size 40 mm × 4 mm × 3 mm.

The high temperature water vapor corrosion test was performed using a Corrosion Testing Machine (Japan Ultra-high Temperature Materials Research Center). The sample was kept on mullite jig and then heated under the following conditions—temperature: 1300 °C for 100 h and 1500 °C for 50 h; gas flow: 30 wt.% water (air:H_2O = 70:30 (wt.%)), gas flow rate: 175 ml/min which is corresponding to

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doi:10.1016/j.ceramint.2004.03.044

the velocity of 4.6×10^{-4} m/s. To exclude the water vapor corrosion occurring at low temperatures, the corrosive gas was introduced when the temperature reached 1500 °C and the gas flow was stopped after the 100 h testing period.

The phase and composition were determined by X-ray diffraction and energy dispersive X-ray (EDX) techniques, respectively.

3. Results and discussion

Because the preparation of mullite bulk in this study was performed in graphite crucible, a small amount of Al_2O_3 phase was formed [6] as shown in Fig. 1. The weights slightly increased during the corrosion test with weight gain rate of 6.60×10^{-6} g/cm^2 h at 1300 °C and 8.42×10^{-5} g/cm^2 h at 1500 °C. This otherwise reveals us that the weight change for 1500 °C test is ten times larger than that for 1300 °C test.

Fig. 2(a) and (b) show X-ray diffraction patterns for the samples surface after corrosion test at 1300 and 1500 °C, respectively. The relative intensities of corundum phase increased after the corrosion test. For the samples after corrosion tested at 1500 °C all peaks corresponded to corundum phase and the mullite phase completely disappeared. Fig. 3 shows the X-ray diffraction pattern of the cross-section of the sample after corrosion tested at 1500 °C. The peaks for mullite phase can be observed and the relative intensities for mullite phase against corundum phase are almost the same as as-sintered, i.e., before testing (Fig. 1). From this, it is recognized that corundum phase was formed only on the bulk surface in water vapor environment at elevated temperatures.

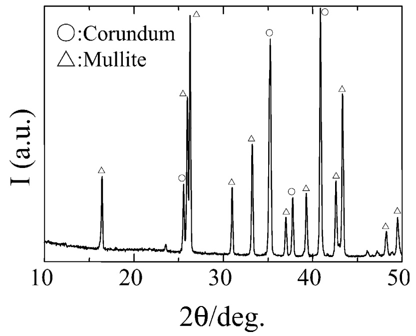

Fig. 1. X-ray diffraction pattern of mullite bulk before the corrosion test.

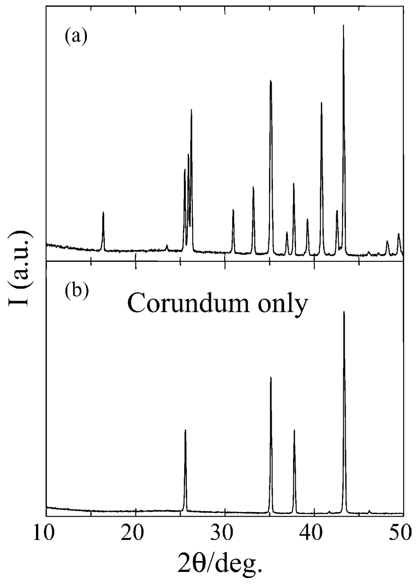

Fig. 2. X-ray diffraction patterns for the test sample surfaces at (a) 1300 °C and (b) 1500 °C.

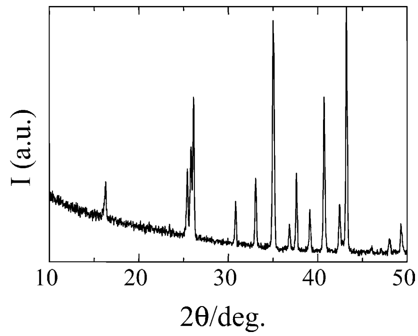

Fig. 3. X-ray diffraction pattern of the cross-section of the test sample at 1500 °C.

Fig. 4(a) and (b) show the SEM images of the mullite samples after corrosion test at 1300 and 1500 °C, respectively. The surfaces in both cases are non homogeneous. EDX analyses were performed in the places that are marked in figures as A and B. The composition of Al_2O_3:SiO_2 in area A and B are 1.0:0.0 and 8.09:1.91, respectively. For calculation, the sample before testing was used as a reference and the composition of Al_2O_3:SiO_2 assumed to be exactly 3:2. From this result, it is recognized that the faceted grains denote pure corundum phase. No other elements can be detected in these areas. The size of corundum grains in area B is small about 1 μm. As the composition of area B contains also silica component, the phase as indicated by arrow in the figure denotes aluminosilicate phase. So, it might be confirmed that pure corundum crystalline grains directly formed from aluminosilicate phase. In some places, holes are observed as indicated by bold arrows in Fig. 4(a) in both cases.

Fig. 5(a) and (b) show SEM images of the cross-section of mullite samples after corrosion test at 1300 and 1500 °C, respectively. Larger pores of size 100 μm are observed in Fig. 5(b) at near the bulk surface. Such large pores are not observed in 1300 °C sample (Fig. 5(a)). The composition of Al_2O_3:SiO_2 of area C in Fig. 5(b) is 3.04:1.98 that is just the same as the reference composition. In other words, the composition of Al_2O_3:SiO_2 retained the same throughout the bulk except at the bulk surface and in the pore area.

Fig. 6 shows the magnified image of a pore (shown in Fig. 5(b)). Faceted grains were observed as in bulk surface. The composition of Al_2O_3:SiO_2 of areas D and E are 1.0:0.04 and

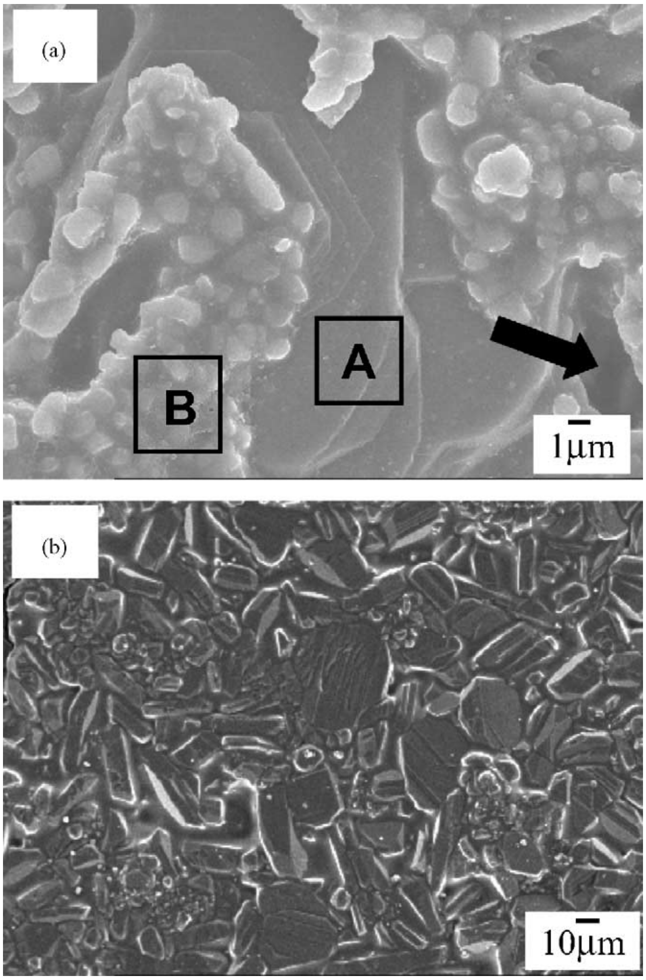

Fig. 4. SEM images of the sample surfaces at (a) 1300 °C and (b) 1500 °C.

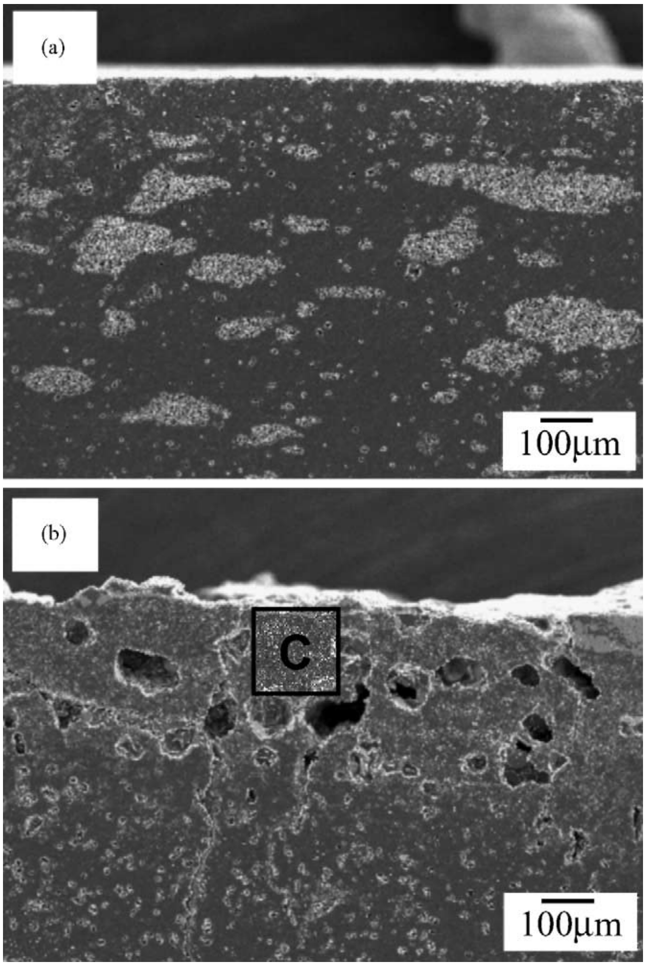

Fig. 5. SEM images of the cross-sections for (a) 1300 °C and (b) 1500 °C testing samples.

1.0:1.85, respectively. From these results, it is concurred that area D corresponds to mainly corundum phase. However, the corundum phase included a small amount of silica component. The corundum phase is directly formed from silica-rich aluminosilicate phase. Because the silica content of the aluminosilicate phase in area E is higher than that before corrosion, it can be considered that the silica-rich aluminosilicate was formed from mullite phase either by corrosion and/or by decomposition of mullite phase. In area E, small amount of sodium element was also detected as shown in the Fig. 6. Although purities of the starting materials of Al_2O_3 and SiO_2 powders were high enough, these powders contained sodium as an impurity in the range of 0.001% for Al_2O_3 powder and 10 ppm for SiO_2 powder. The surface of area E is very smooth, just like as melted surface. No sodium element was observed in area D.

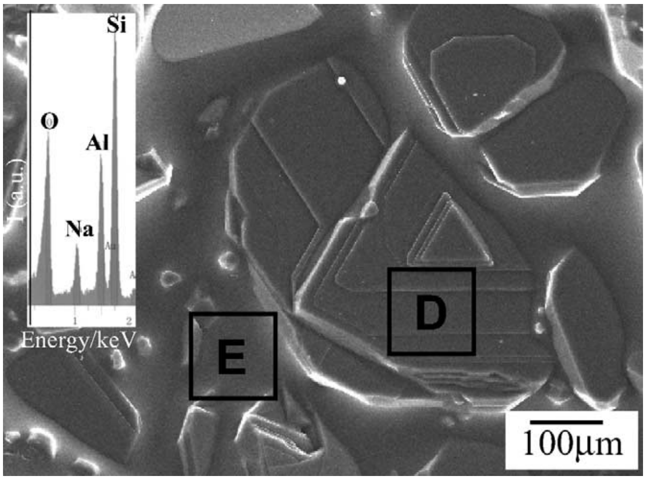

Fig. 6. SEM image of a inside of pore.

For the reason that some pores can be observed in the sample surface after corrosion test as shown in Fig. 4(a), it is considered that the pores formed in the sample tested at 1500 °C (as shown in Fig. 5(b)) are associated with the sample surface, namely, open pores are generated by corrosion of mullite phase. Such pores can not be observed in 1300 °C sample as shown in Fig. 5(a), so the surface area for 1500 °C would be larger than that of 1300 °C sample. Corundum phase was generated at all surfaces as shown in Figs. 4 and 6.

Tai et al. [7] reported that the weight of Al_2O_3 phase increased in water vapor environment at high temperatures, even if the boundary phase was corroded and removed. That is, water vapor diffuses into alumina lattice from the grain surface. In other words, at high temperatures the corundum phase is actually corroded by water vapor according to Eq. (1), in which case, the weight decreases. However, the corundum phase can absorb water molecule according to Eq. (2), to result in the weight increase. In previous report [7], the corundum phase was reported to have weight gain by water vapor corrosion test. Thus, in the water vapor corrosion of corundum phase, the increasing weight is larger than the decreasing weight at high temperatures, especially, above 1500 °C. This is attributed to the larger surface area of 1500 °C sample than that of 1300 °C sample due to the formation of open pores as shown in Fig. 5(b), and also, the amount of corundum phase that generated on the mullite or aluminosilicate surface for 1500 °C sample is larger than that of 1300 °C sample. From this, it can be explained that the apparent weight change of 1500 °C sample is much larger than that of 1300 °C sample.

$$\mathrm{Al_2O_3(s) + 3H_2O(g) = 2Al(OH)_3(g)} \qquad (1)$$

$$\mathrm{Al_2O_3(s)} + n\mathrm{H_2O(g) = Al_2O_3} \cdot n\mathrm{H_2O(s)} \qquad (2)$$

Moreover, in the hot corrosion experiments, when there is even a little amount of sodium, silica phase reacts with sodium oxide and sodium silicate is easily formed [3,4]. The melting points of sodium silicates are lower than 1000 °C. So, it is considered that silica-rich boundary phase reacts with impurity sodium oxide and silica rich aluminosilicate is formed. The silica rich aluminosilicate with sodium element melts well below 1300 and/or 1500 °C. It is well known that silica phase is easily corroded by water vapor at high temperatures [8] and the water vapor corrosion rate of silica is accelerated by hydroxide ions [9]. So, it is easy to consider in present case that silica component in the liquid state silica rich aluminosilicate phase was volatilized by water vapor according to Eq. (3).

$$\mathrm{Al_2O_3} \cdot y\mathrm{SiO_2(l)} + 2y\mathrm{H_2O(g)} = y\mathrm{Si(OH)_4} + \mathrm{Al_2O_3(s)} \qquad (3)$$

Along these lines, the concentration of alumina component in liquid aluminosilicate phase will be high during the progression of Eq. (1) and sodium oxide component will be also condensed by progression of Eq. (3). As a consequence, excess corundum is deposited from aluminosilicate liquid phase as shown in Fig. 6. Therefore, it is considered that the formation of liquid aluminosilicate phase, corrosion of silica component by water vapor (Eq. (3)) and deposition of corundum phase are accelerated by concentrated sodium oxide. And then, surface of mullite bulk was completely covered with corundum phase as shown in Fig. 2.

4. Conclusion

By the static state water vapor corrosion at high temperatures as 1300 and 1500 °C, mullite bulk was covered with corundum phase. The weights of the samples were slightly increased during the corrosion test. It is speculated that the existing impurity sodium oxide, liquid state aluminosilicate containing sodium oxide is formed and that the volatilization of silica component from the liquid phase by water vapor attack is accelerated to deposit corundum phase from the liquid phase.

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